MIT-CTP-4424

Effective Field Theory for Supercooled Liquids

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Starting from a microscopic model of liquids, we construct an effective theory of the overlap field for the doubly-replicated system through coarse-graining. We then establish a recipe to extract a relaxation time and two characteristic length scales of a supercooled liquid from this effective field theory. Appealing to the Ginzburg-Landau-Wilson paradigm near the putative critical point, we conclude that the scalings of these quantities are concealed in models belonging to the Ising universality class.

Conventional wisdom envisions emergent diverging length scales in a supercooled liquid near its Kauzmann temperature [1], underlying dramatic dynamical slowdown [2]. Despite the ethereal nature of these length scales, recent advances both in experiments and numerical simulations are starting to expose them to our naked eyes, manifested in the form of dynamical heterogeneities [3, 4]. In this paper, we construct a quantitative theory of supercooled liquids, embracing the divergences of emergent length scales at the putative critical temperature T_0 as the organizing principle.

Let us first sketch the physics of supercooled liquids, to be fortified by our formalism. When a liquid is sufficiently cooled, each constituent particle is caged by its neighbors and vibrates around its itinerant center [5]. Occasionally a collection of particles, spanning a region of linear size $\xi_{\rm CRR}$, cooperatively rearrange to access a distinct amorphous configuration [2]. Orchestrations of these events, taking place at a larger length scale $\xi_{\rm M}$ [6], relax the system by wiping out its coarse memory, namely, significant resemblance to its initial configuration. We presume that the lower the temperature, the fewer the accessible amorphous configurations, the larger the cooperatively rearranging regions, the grander the orchestrations, and the longer the relaxation time τ_α.

Our plan of attack is as follows. We first take two identical systems and put them in similar configurations whose resemblance is quantified by an overlap field. Evolving in time, the two systems look alike for a while. Eventually, however, small differences in their initial conditions – be they in positions or in momenta – get amplified until their resemblance is completely lost. This departure takes place when the two systems lose their coarse memories on the time scale τ_α. We can identify this time scale by following the evolution of the overlap field, coarse-graining all the other microscopic information away. The resulting effective field theory, when complemented by appropriate stochastic dynamics, encodes τ_α. As we shall see, the size of cooperatively rearranging regions $\xi_{\rm CRR}$ is imprinted on this effective field theory as the static correlation length. When this length scale diverges, the effective theory of the overlap field provides a universal description of critical phenomena in supercooled liquids, which we now pursue.

For concreteness, let us consider s species of classical particles governed by a many-body Hamiltonian

$$H_{\rm o}\left[\{\mathbf{x}_i^a\},\{\mathbf{p}_i^a\}\right]=\sum_{a=1}^{s}\left\{\sum_{i=1}^{N_a}\frac{\left(\mathbf{p}_i^a\right)^2}{2m_a}\right\}+v\left[\{\mathbf{x}_i^a\}\right], \tag{1}$$

confined in a box of d-dimensional volume V. We then introduce an exact replica governed by

$$H_{\rm r}\left[\{\mathbf{y}_i^a\},\{\mathbf{q}_i^a\}\right]=\sum_{a=1}^{s}\left\{\sum_{i=1}^{N_a}\frac{\left(\mathbf{q}_i^a\right)^2}{2m_a}\right\}+v\left[\{\mathbf{y}_i^a\}\right] \tag{2}$$

and define a total overlap

$$O\left[\{\mathbf{x}_i^a\},\{\mathbf{y}_i^a\}\right]=\sum_{a=1}^{s}\left\{\sum_{i,j=1}^{N_a}w\left(\frac{|\mathbf{x}_i^a-\mathbf{y}_j^a|}{l_a}\right)\right\} \tag{3}$$

to characterize its configurational resemblance to the original system. Here we take l_a to be of the order of the average interatomic distance around a particle of a-species and $w(z)$ to be a monotonically decreasing smooth function with $w(0)=1$ and $w(z)=0$ for $z\geq 1$: we expect details of these choices to be washed away in the spirit of universality. The next step is to consider the partition function [7–11]

$$Z\left(\beta,g_{\rm r}\right)={\rm Tr}\left[e^{-\beta(H_{\rm o}+H_{\rm r})+g_{\rm r}O}\right] \tag{4}$$

as a mathematical construct from which we extract physics. As usual the trace is the integration over positions and momenta [divided by $\prod_a\left(N_a!\right)^2$] and we tacitly exclude the crystalline phase space from it [23].

We now coarse-grain the system à la Kadanoff by dividing the whole volume into hypercubic blocks $b(\mathbf{l})$ of linear size $l_{\rm cut}$, labeled by a lattice variable $\mathbf{l}$. To each block we associate an overlap field

$$\begin{aligned}&\check{\phi}_{\mathbf{l}}\left[\{\mathbf{x}_i^a\},\{\mathbf{y}_i^a\}\right]\\ &=\frac{1}{2\rho l_{\rm cut}^d}\sum_{a=1}^{s}\Bigg[\left\{\sum_{\mathbf{x}_i^a\in b(\mathbf{l})}\sum_{j=1}^{N_a}w\left(\frac{|\mathbf{x}_i^a-\mathbf{y}_j^a|}{l_a}\right)\right\}\\ &\quad+\left\{\sum_{\mathbf{y}_i^a\in b(\mathbf{l})}\sum_{j=1}^{N_a}w\left(\frac{|\mathbf{y}_i^a-\mathbf{x}_j^a|}{l_a}\right)\right\}\Bigg]\end{aligned} \tag{5}$$

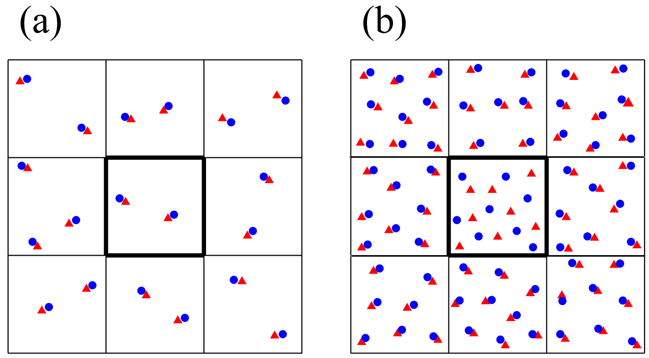

FIG. 1: A block surrounded by blocks with high overlap. Dots indicate particles of the original system and triangles indicate those of the replica. (a) Below the scale $\xi_{\rm CRR}$, the pinning effect is dominant and we expect high overlap in the middle block. (b) Above the scale $\xi_{\rm CRR}$, the centers of particles in the middle block are unpinned and we expect low overlap on average.

where the overall density $\rho = \sum_{a=1}^{s} N_a/V$. Note that $O = \rho\, l_{\rm cut}^d \sum_{\bf l} \check{\phi}_{\bf l}$. Regarding the overlap field as the only order parameter to follow, we integrate out all the other microscopic degrees of freedom. Inserting $1 = \int \prod_{\bf l} d\phi_{\bf l} \delta\left(\phi_{\bf l} - \check{\phi}_{\bf l}\right)$ and interchanging the order of the integrations, we obtain

$$Z(\beta, g_{\rm r}) = {\rm Tr}\left[\int \prod_{\bf l} d\phi_{\bf l}\delta\left(\phi_{\bf l} - \check{\phi}_{\bf l}\right) e^{-\beta(H_{\rm o}+H_{\rm r})+g_{\rm r}O}\right]$$
$$= \int \prod_{\bf l} d\phi_{\bf l} \exp\left(-\beta\mathcal{H}_\beta^\Lambda\left[\{\phi_{\bf l}\}\right] + g_{\rm r}^\Lambda \sum_{\bf l} \phi_{\bf l}\right) \quad (6)$$

with $g_{\rm r}^\Lambda = \rho l_{\rm cut}^d g_{\rm r}$ and

$$e^{-\beta\mathcal{H}_\beta^\Lambda[\{\phi_{\bf l}\}]} = {\rm Tr}\left[\left\{\prod_{\bf l} \delta\left(\phi_{\bf l} - \check{\phi}_{\bf l}\right)\right\} e^{-\beta(H_{\rm o}+H_{\rm r})}\right]. \quad (7)$$

Changes in the cutoff scale $\Lambda = 1/l_{\rm cut}$ induce the renormalization group flow for this effective field theory.

Having constructed the effective theory of the overlap field, we analyze how it encodes characteristic scales of a single supercooled liquid. First consider the linear size of cooperatively rearranging regions $\xi_{\rm CRR}$, envisaged by Adam and Gibbs [2]. Above this scale, particles in a block can access distinct amorphous configurations while keeping particles outside the block essentially unaffected; below this scale, a distribution of particles around a block pins down the centers of particles inside the block. Within a given block in the doubly-replicated system, particles of the original system and those of the replica feel virtually the same external potential so long as the block of interest is surrounded by blocks with high overlap between the two systems, measured by the overlap field (see Fig.1). We expect to observe high overlap in the block of interest below the scale $\xi_{\rm CRR}$ and low overlap above it, in the absence of the replica coupling $g_{\rm r}$.

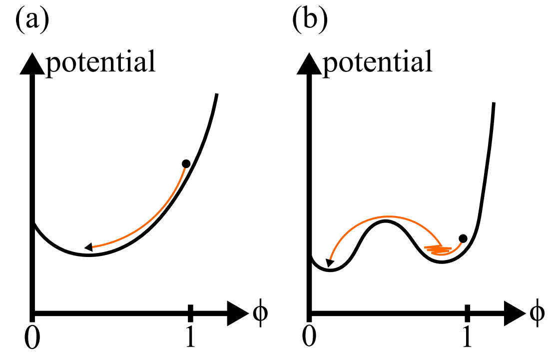

FIG. 2: The potential term in the effective Hamiltonian (a) with no metastable minimum and (b) with a metastable minimum. Also depicted for each case is a typical trajectory starting with high overlap and ending with low overlap.

The resulting shift from high to low overlap is also what we expect on the correlation length scale of the overlap field. We thus take the static correlation length of the effective field theory at $g_{\rm r} = 0$ as a proxy for $\xi_{\rm CRR}$.

Turning our attention to the relaxation time scale τ_α, let us examine how the two decoupled systems at $g_{\rm r} = 0$ lose their initial resemblance with high overlap. To this end it is useful to consider the potential term in the effective Hamiltonian $\mathcal{H}_\beta^\Lambda$ for the overlap field ϕ. If this potential had no metastable minimum, the overlap field would slowly cascade down the hill [see Fig.2(a)]. It would then be hard, however, to attain dramatic slowdown with modest changes in the correlation length, which is the characteristic phenomenology of supercooled liquids. Hence we instead suppose that the potential has a metastable state – call this a replica-locking state – in which the resemblance is retained for a long while [see Fig.2(b)]. (We shall come back to this hypothesis later.) Eventually the overlap field jumps over the potential barrier via thermal activation, reaching what we call a free-sampling state where particles in the two systems move in an uncorrelated manner without any resemblance. The lifetime of the metastable replica-locking state at $g_{\rm r} = 0$ then codifies the relaxation time τ_α. In passing, we note that turning on the replica coupling $g_{\rm r}$ tilts the potential and induces a first-order phase transition at $g_{\rm r} = g_{\rm r,1}(T) > 0$ for $T > T_0$ [9], beyond which the replica-locking state becomes stable.

Finally along with jumps from the metastable replica-locking state to the stable free-sampling state comes another length scale, namely, the size of thermal instantons describing erasure of the coarse memory. It represents the typical size of orchestrations needed to relax the supercooled liquid, $\xi_{\rm M}$, emphasized by Biroli and Bouchaud [6]: without such mega rearrangements, the system keeps revisiting its previous configurations (see Fig.3). The same concept is encapsulated as mosaic patches in the random first-order transition theory [12, 13] and as metabasins in the potential-energy landscape picture [14–16].

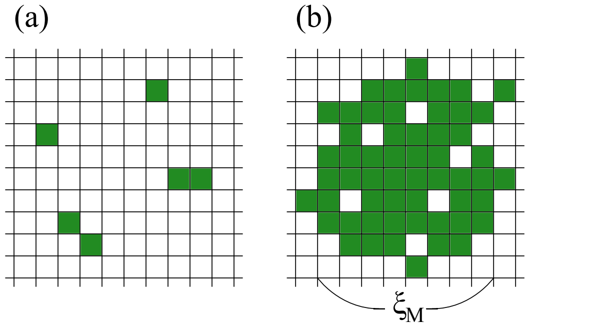

FIG. 3: The system divided into blocks of the size $\xi_{\rm CRR}$, with shades indicating cooperative rearrangements with respect to a given initial configuration. (a) Sparse cooperative rearrangements are not enough to wipe out the coarse memory. (b) After orchestrated cooperative rearrangements, the system has negligible probability to revisit its past.

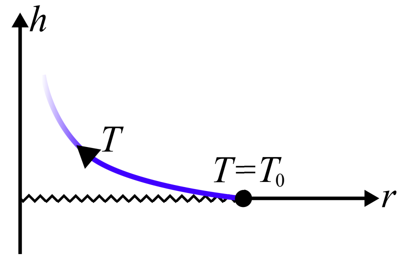

FIG. 4: A schematic picture of the $g_{\rm r}=0$ line projected onto the relevant parameter space of the Ising universality class, valid near the critical point. The dot denotes the unstable Ising fixed point where $(r,h)=(0,0)$ and the zigzag line marks the first-order phase transitions.

Given the dictionary between the single supercooled liquid and the effective theory of the overlap field for the doubly-replicated system, our remaining task is to develop the latter machinery to the point where we can perform calculations. To do so, first recall that the number of accessible amorphous configurations decreases as we lower the temperature and gets depleted near the Kauzmann temperature [1]. As we have seen, this phenomenology is realized when the correlation length of the effective field theory at $g_{\rm r}=0$ – an avatar of the size of cooperatively rearranging regions $\xi_{\rm CRR}$ – diverges. Therefore we presume that the correlation length diverges at $(T,g_{\rm r})=(T_0,0)$, the putative critical point. Given that the effective field theory has the one scalar field ϕ, the two relevant intensive variables $(T,g_{\rm r})$, and the diverging static correlation length $\xi_{\rm CRR}$, the Ginzburg-Landau-Wilson principle then leads us to conclude that the theory lies in the Ising universality class. In particular its universal features are captured by the Ising model with the near critical temperature $r\sim T^{\rm Ising}-T_{\rm c}^{\rm Ising}$ and the external magnetic field h. Under this identification, the parameters $r=r(T,g_{\rm r})$ and $h=h(T,g_{\rm r})$ are analytic functions of the intensive variables $(T,g_{\rm r})$ [17] and vanish at the critical point.

To proceed further, we must identify where the effective field theory with $g_{\rm r}=0$, from which we extract observables of the single supercooled liquid, lies in the relevant parameter space of the Ising universality class. With the anticipation of the diverging correlation length at $(T,g_{\rm r})=(T_0,0)$ and of the first-order phase transitions at $g_{\rm r}=g_{{\rm r},1}(T)>0$ for $T>T_0$, we arrive at the schematic picture depicted in Fig.4. To determine the shape of the $g_{\rm r}=0$ line, first note that the variable $g_{\rm r}$ linearly couples to the overlap field [cf. Eq.(6)]. In turn it affects only $h(T,g_{\rm r})$ and thus we set $r(T,g_{\rm r})=r(T)$. Second we stipulate, as is customary, that the change of variables from the intensive variables $(T,g_{\rm r})$ to the parameters (r,h) is nonsingular at the critical point $(T,g_{\rm r})=(T_0,0)$. From these two requirements, combined with the analyticity, it then follows that $r\big|_{g_{\rm r}=0}\sim-\Delta T$ and $h\big|_{g_{\rm r}=0}\sim(\Delta T)^n$ with $\Delta T=T-T_0$ and a positive integer n. Note that, to ensure the metastability as mentioned before, we set $n\geq 2$: setting $n=1$ would result in the power-law scaling of the relaxation time as in standard dynamic critical phenomena [18].

In the companion paper [19], for each value of $n\geq 2$, we compute the critical exponents defined via $\xi_{\rm CRR}\sim\Delta T^{-\nu}$, $\log(\tau_\alpha)\sim\Delta T^{-\zeta}$, and $\xi_{\rm M}\sim\Delta T^{-\theta}$. At the end of the day, choices of n and the whole formalism developed herein are justified (or falsified) a posteriori when we turn the crank of the machinery and compare to experiments.

We elucidated a systematic way to cast the physics of supercooled liquids under the framework of the renormalization group. There emerged two characteristic length scales, the size of cooperatively rearranging regions $\xi_{\rm CRR}$ and the size of mega rearrangements $\xi_{\rm M}$: the former is static and the latter is dynamic [20]. To obtain the detail-independent description for salient features of supercooled liquids [21], it was essential to assume that the static length scale $\xi_{\rm CRR}$ diverges as we approach the putative critical point. Indeed we could have instead imagined scenarios in which only $\xi_{\rm M}$ [22], or no length scale, would diverge. In doing so, however, we would essentially give up a notion of nontrivial universality in the physics of supercooled liquids.

The author first would like to thank Ethan S. Dyer and Jaehoon Lee for their zeal in field theories, which facilitated the conception of this paper and led to our collaboration. He is indebted to Allan W. Adams, Shamit Kachru, and John A. McGreevy for stimulating discussions. He also wishes to express his gratitude to the participants, especially the principle organizer Giulio Biroli, of the 2012 Beg Rohu Summer School "Glass and Jamming Transitions" for their welcoming atmosphere. He finally would like to thank Gilles Tarjus for introducing him to the world of supercooled liquids as a guest speaker for Steven A. Kivelson's group meeting. He is supported by a JSPS Postdoctoral Fellowship for Research Abroad.

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